

Steam effect on NO_x reduction over lean NO_x trap Pt–BaO/Al₂O₃ model catalyst

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The effect of steam on NO_x reduction over lean NO_x trap (LNT) Pt–Ba/Al₂O₃ and Pt/Al₂O₃ model catalysts was investigated with reaction protocols of rich steady-state followed by lean–rich cyclic operations using CO and C₃H₈ as reductants, respectively. Compared to dry atmosphere, steam promoted NO_x reduction; however, under rich conditions the primary reduction product was NH₃. The results of NO_x reduction and NH₃ selectivity versus temperature, combined with temperature programmed reduction of stored NO_x over Pt–BaO/Al₂O₃ suggest that steam causes NH₃ formation over Pt sites via reduction of NO_x by hydrogen that is generated via water gas shift for CO/steam, or via steam reforming for C₃H₈/steam. During the rich mode of lean–rich cyclic operation with lean–rich duration ratio of 60 /20 s, not only the feed NO, but also the stored NO_x contributed to NH₃ formation. The NH₃ formed under these conditions could be effectively trapped by a downstream bed of Co²⁺ exchanged Beta zeolite. When the cyclic operation was switched into lean mode at $T < 450$ °C, the trapped ammonia in turn participated in additional NO_x reduction, leading to improved NO_x storage efficiency.

KEY WORDS: lean NO_x trap; NO_x reduction; Pt–BaO/Al₂O₃ catalyst; NH₃; steam; cobalt-exchanged beta zeolite.

1. Introduction

Lean burn engines, such as diesel and lean burn gasoline engines, improve the fuel economy and reduce emissions. A major challenge for the usage of lean burn engines is the NO_x aftertreatment because under lean conditions the currently widely used three-way emissions catalyst (TWC) is not effective in eliminating NO_x. Lean NO_x trap (LNT) catalysts provide one of the promising options to reduce lean NO_x for lean burn gasoline engines, with the engine working under so-called lean–rich repeatable operation cycles [1]. Typical cycles consist of a longer lean period, followed by a shorter rich period. Over typical LNT catalysts containing Pt and BaO, it is known that NO is oxidized to NO₂ on the Pt sites, and the NO₂ is then trapped by the Ba species to form barium nitrate during the long period of lean cyclic mode. During the subsequent short rich period, the nitrate decomposes and the released NO_x is reduced to N₂ on the Pt sites by reducing agents in the exhaust [2]. A recent review [3] describes the extensive efforts to study NO oxidation, NO/NO₂ storage, release of nitrate, and the reduction of NO_x over LNT Pt–Ba/Al₂O₃ model catalyst for elucidating NO_x storage/reduction mechanisms and optimizing the storage component loading. In addition, some studies of the release of trapped NO_x have been carried out to understand the mechanism and the reducing ability of different reductants [3]. However, the results reported in the literatures are not consistent with regard to the

released product composition. It is generally believed that NO_x reduction into N₂ occurs during the rich period [3]. Under reducing atmospheres of CO, C₃H₆, or H₂, the released products were found to contain NO_x (NO and NO₂), while other N-containing compounds like NH₃ were not observed during TPD over BaO/Al₂O₃ [4] and even during TPD-FTIR over Pt–Ba/Al₂O₃ [5]. However, very recent TPD/TPR experiments showed that when H₂ was used as the reductant in a dry environment, NH₃ was one of the gases evolved during the release of stored NO_x [6, 7]. NH₃ formation was also observed during transient NO_x reduction with lean–rich cyclic modes over Pt–BaO/Al₂O₃ model catalyst when H₂ was used as reductant [8].

In fact, already in the 1970's studies on the catalytic reduction of NO by H₂ or a mixture of H₂/CO over Pt catalysts had been carried out for the TWC application in automotive exhaust control [9–11]. NH₃ was observed as a major product and the presence of CO strongly inhibited NO reduction over Pt [9]. The formation of NCO groups by the interaction of NO and CO seems well established, but the mechanism of the formation of NH₃ by reduction of NO with CO has been vigorously disputed in accounting for whether the hydrolysis of NCO intermediates provides a major pathway to NH₃. Specifically, it is an issue whether active Pt or support Al₂O₃ plays the catalytic role for the hydrolysis of NCO groups [11–15]. Very recently, experiments conducted by Cant *et al.* for the NO reduction by CO over supported Pt and Pd catalysts showed that the product distribution was strongly influenced by the presence of water. HNCO and NH₃ became the dominant products leaving

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the Pt surface, and Al₂O₃ caused the complete hydrolysis of HNCO to NH₃ if water was in excess over Pt/Al₂O₃ [16]. This is in agreement with the results and interpretation of Voorhoeve *et al.* for the reduction of NO by CO/H₂ over Pt/Al₂O₃ catalyst in the presence of water vapor [17]. The reaction of a NO/CO/H₂O mixture over Pt/Al₂O₃ formed NH₃ with >80% yield, and the presence of NH₃ also promoted the formation of HNCO that in turn resulted in the amplification of NH₃ [18]. Furthermore, if the feed contained more CO, there was a greater amplification of NH₃ because of the intervention of the water gas shift reaction over Pt/Al₂O₃ [19].

Steam is one of major components in automotive emissions due to fuel combustion. The steam effects on the effectiveness of TWC catalysts have been widely investigated [20, 21]. However, the nature of the steam effect on NO_x reduction over LNT catalysts has not been extensively explored [22], particularly under lean–rich cyclic operations [8]. Furthermore, although NH₃ is currently not a regulated emission by EPA, excess ammonia emissions from a vehicle fleet could pose a serious problem for air quality in urban areas because ammonia emissions react in the atmosphere with the nitric acid produced in photochemical smog to yield fine particle ammonium nitrate [23]. It is also interesting to consider the formation of NH₃ during the NO_x reduction over LNT catalyst in view of potential use of H₂ in future H₂ internal combustion engines (ICE).

In the work reported here, we investigated the effect of steam on the product composition of NO_x reduction obtained during the rich period over LNT Pt–BaO/Al₂O₃ and Pt/Al₂O₃ model catalysts. We also describe how the NH₃ generated over Pt–BaO/Al₂O₃ during the rich cycle can be removed using a dual-bed reactor system containing Co²⁺/Beta zeolite in a down-stream bed.

2. Experimental

Around 1.0%Pt/Al₂O₃ (w/w) was prepared by impregnation of γ-Al₂O₃ (Alcoa World Chemical, SA = 250 m²/g) with H₂PtCl₄ aqueous solution. The as-prepared H₂PtCl₄/Al₂O₃ was dried in an oven overnight at 80–90 °C and then at 120 °C for 24 h. Finally, Pt/Al₂O₃ was obtained through heating H₂PtCl₄/Al₂O₃ up to 500 °C in a 5%H₂/N₂ flow for 4 h before loading barium nitrate precursor solution. The Pt dispersion on Al₂O₃ was 43%. The dispersion was measured by CO chemisorption at 25 °C on a Quantachrome CHEMBET-3000 instrument, and based on the assumption that one CO molecule adsorbs on one Pt atom site. Pt–Ba(NO₃)₂/Al₂O₃, the precursor of LNT Pt–BaO/Al₂O₃ model catalyst, was obtained by impregnating a barium nitrate (Aldrich, +99%) solution onto Pt/Al₂O₃ powder with an equivalent BaO to Al₂O₃ ratio of 0.15 (dry base

w/w), followed by drying in an oven at 120 °C for 24 h. The solid Pt–Ba(NO₃)₂/Al₂O₃ was pressed, crushed, and sieved. Using mesh size 40–60, an amount of Pt–Ba(NO₃)₂/Al₂O₃ equivalent to 100 mg of Pt–BaO/Al₂O₃ was mechanically mixed with 100 mg of cordierite ceramic with the same mesh size, and then placed into a quartz reactor with plugs of quartz wool on both sides. The Pt–BaO/Al₂O₃ catalyst was obtained by *in-situ* heating of Pt–Ba(NO₃)₂/Al₂O₃ at 600 °C for 2 h under a 5%CO/N₂ flow, prior to commencing lean–rich cyclic operations.

The reduction of NO_x as a function of temperature was measured first in a dry atmosphere, and then again in presence of steam with the same reductant. Under either atmosphere, two types of reaction protocols, rich steady-state, then followed by lean–rich cyclic operations, were carried out at different temperatures. Reaction protocols were set by a time controller through adjusting the time ratio of lean to rich (L/R) to introduce a lean flow or a rich flow into the reactor system. The lean–rich cyclic operations were performed by adjusting L/R in the range from 60/20 to 60/1800 (s/s), whereas the rich steady-state condition was obtained by setting the lean period to zero. The reactor feed, having a total flow rate of 750 cm³ min^{−1} (STP), consisted of a 500 cm³ min^{−1} (STP) main stream that was mixed with either a 250 cm³ min^{−1} (STP) lean (O₂/N₂) flow to form a lean feed stream, or with a 250 cm³ min^{−1} (STP) rich (CO/N₂ or C₃H₈/N₂) flow to form a rich feed stream. The main stream contained mixed flows of NO/N₂, CO₂/N₂, and steam/N₂. The steam/N₂ flow was generated by metering water with a pump into a heated N₂ flow. Thus, the reactor inlet gas mixture during the lean cyclic mode consisted of 500 ppm NO, 5% O₂, 10% CO₂, 10% H₂O, and balance N₂. The rich cyclic mode consisted of 500 ppm NO, 1.7% CO (or 3300 ppm C₃H₈), 10% CO₂, 10% H₂O, and balance N₂. The space velocity (SV) corresponding to 100 mg Pt–Ba/Al₂O₃ catalyst equaled 225,000 h^{−1}. The gas compositions at the inlet and outlet of the reactor were analyzed by a CIMS analyzer (Multi Component Gas Analyzer of V&F Analysetechnik Airsense 2000).

The NO reduction conversion and the selectivity to NH₃ during the rich steady-state were calculated from the concentrations of inlet NO and outlet NO, according to

$$\text{NO(R)} = [(\text{NO}(\text{inlet}) - \text{NO}_x(\text{outlet}))/\text{NO}(\text{inlet})] \times 100\%$$

and

$$\text{S}_{\text{NH}_3}(\text{R}) = [\text{NH}_3(\text{outlet})/(\text{NO}(\text{inlet}) - \text{NO}_x(\text{outlet}))] \times 100\%$$

Under lean–rich cyclic operations, the exit gas concentration was recorded for about 20 min after the cyclic operation had stabilized. The NO_x conversion and NH₃

selectivity were calculated for each cycle, and then averaged over at least 5 cycles under stabilized lean–rich conditions. The NO_x removal efficiency, i.e. the NO_x storage efficiency of the lean period, was calculated by

$$\text{NO}_x(\text{L}/(\text{L} + \text{R})) = \left[\frac{\int \text{NO}(\text{Inlet}) - \int \text{NO}_x(\text{Outlet})}{\int \text{NO}(\text{Inlet})} \right] \times 100\%$$

However, when switching to the rich mode, the inlet amount of NO_x should include both the feed NO and the released NO_x that is stored in the LNT catalyst during the lean period, and hence the NO_x conversion during the rich period should be represented by

$$\begin{aligned} \text{NO}_x(\text{R}/(\text{L} + \text{R})) \\ = \left[\frac{\int \text{NO}_x(\text{Release}) + \int \text{NO}_x(\text{Inlet}) - \int \text{NO}_x(\text{Outlet})}{\int \text{NO}_x(\text{Release}) + \int \text{NO}_x(\text{Inlet})} \right] \times 100\% \end{aligned}$$

The selectivity of NO_x conversion to NH₃ during the rich period should be represented by

$$\begin{aligned} \text{S}_{\text{NH}_3}(\text{R}/(\text{L} + \text{R})) \\ = \left[\frac{\int \text{NH}_3(\text{Formation})}{\int \text{NO}_x(\text{Release}) + \int \text{NO}_x(\text{Inlet}) - \int \text{NO}_x(\text{Outlet})} \right] \times 100\% \end{aligned}$$

Temperature-programmed reduction (TPR) under H₂ atmosphere (5% H₂/N₂) was carried out on NO₂-exposed Pt–BaO/Al₂O₃. Thermogravimetry (TG) coupled with infrared spectrometry (IR) was used to measure the mass loss and to determine the composition and concentrations of the evolved gases. The detailed procedures for NO₂ exposure and NO_x release were described in our previous work [24]. Briefly, prior to NO₂ storage, Pt–Ba(NO₃)₂/Al₂O₃ was heated to 800 °C for 0.1 h in a He flow followed by cooling down to 25 °C. Then, the sample was exposed to a gas flow consisting of 1.0 % (v/v) NO₂, 2.8 % O₂ with balance N₂ for 15 min. TG-IR of the NO_x-stored sample was performed on a Perkin–Elmer TGA-7 TG analyzer and a Perkin–Elmer FT-IR SPECTRUM 2000 with KBr optics. The TGA heating ramp ($r = 10 \text{ }^\circ\text{C min}^{-1}$) was synchronized with the scanning (one scan per 0.06 min) of infrared spectra of gases evolved from the TGA. The real time spectra with a resolution of 8 cm^{−1} were collected using TimeBase software in the range between 4000–450 cm^{−1}.

3. Results and discussion

3.1. Rich steady NO reduction over Pt/Al₂O₃ and Pt–BaO/Al₂O₃

The NO reduction by CO under rich steady-state was first investigated in the absence of steam over Pt/Al₂O₃ and LNT Pt–BaO/Al₂O₃ model catalyst, respectively. As shown in figure 1a, no NH₃ formation was detected.

The presence of BaO promotes NO conversion because the light-off temperature (defined as the temperature where 50% NO conversion was reached) over Pt–BaO/Al₂O₃ was at approximately 430 °C, much lower than that of Pt/Al₂O₃ (557 °C). At 500 °C, Pt–BaO/Al₂O₃ gave complete NO conversion, while Pt/Al₂O₃ gave only 22% NO conversion.

Once steam was added, a significant increase in NO reduction was observed. The light-off temperature decreased to 290 °C over Pt–BaO/Al₂O₃, and 320 °C over Pt/Al₂O₃. Compared to dry conditions, the BaO promotion effect was much less pronounced. Interestingly, the presence of steam did not increase the NO conversion in the low temperature region (i.e. ~260 °C), where under both conditions a limited amount of NO conversion was observed.

However, the improvement of NO reduction under steam condition was accompanied by significant NH₃ formation. Figure 1b compares the rich NO conversion and the NH₃ selectivity in presence of steam over Pt–BaO/Al₂O₃ catalyst when CO and C₃H₈ were used as reductants, respectively. When CO was used as reductant in the temperature range below 500 °C over both Pt/Al₂O₃ and Pt–BaO/Al₂O₃ catalysts, 90% of the reduction product was NH₃. With further increase of reaction temperature to 600 °C, the NH₃ selectivity gradually decreased to 65% over Pt/Al₂O₃ and to 43% over Pt–BaO/Al₂O₃, respectively. When C₃H₈ was used as reductant, the NO conversion as function of temperature was very similar to that observed for CO. But in striking contrast with CO, no NH₃ formation was detected until 320 °C, and then the ammonia selectivity increased with increasing temperature.

3.2. NO_x reduction over Pt–BaO/Al₂O₃ under lean–rich cyclic operations

Lean–rich cyclic operations were performed over LNT Pt–BaO/Al₂O₃ model catalyst to evaluate the non-steady state reduction characteristics, with focus on the effect of steam during the rich cycle period. Figure 2a shows the outlet gas concentration for lean–rich cycles of L/R = 60/20 (s/s) at the reaction temperature of 360 °C. During the lean period, both NO and NO₂ were detected in the outlet stream, and the concentration of NO₂ was higher than NO although only NO was fed in the inlet flow. This shows that Pt-catalyzed oxidation of NO into NO₂ occurred. During the lean mode, the NO₂ concentration should depend on the NO oxidation rate, the thermodynamic equilibrium of NO/NO₂, and the NO₂ diffusion and storing rate on BaO. Only trace concentrations of NH₃ were measured at the beginning of the lean period. Then NH₃ concentration gradually decreased to zero towards the end of the lean cycle period. When switching from lean to rich conditions, the total NO_x to be reduced consisted of 500 ppm NO in the feed and additional NO_x released from Ba(NO₃)₂ in

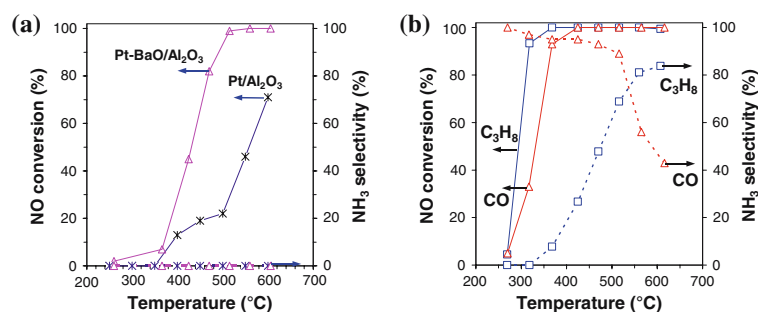


Figure 1. (a) NO conversion (solid line) and NH_3 selectivity (dashed line) over $\text{Pt/Al}_2\text{O}_3$ (*) and $\text{Pt-BaO/Al}_2\text{O}_3$ (Δ) catalysts under dry, rich steady-state conditions with CO as reductant; (b) Comparison of NO conversion (solid line) and NH_3 selectivity (dashed line) over $\text{Pt-BaO/Al}_2\text{O}_3$ catalyst under steam, rich-steady conditions with CO (Δ) or C_3H_8 (\square) as reductant.

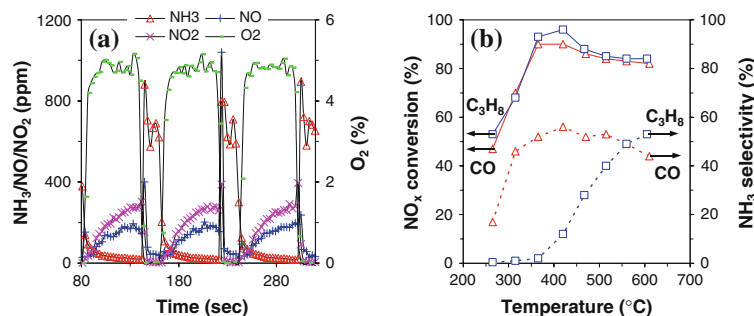


Figure 2. (a) Exit gas concentration of stabilized lean–rich cycles at 360 °C for NO_x trapped and reduced by CO over $\text{Pt-BaO/Al}_2\text{O}_3$ catalyst using lean (500 ppm NO –10% H_2O –10% CO_2 –5% O_2 –balance N_2) and rich (500 ppm NO –10% H_2O –10% CO_2 –1.7% CO –balance N_2) cycles ($\text{L/R} = 60/20$ s); (b) NO_x conversion (solid line) and NH_3 selectivity (dashed line) during rich period over $\text{Pt-BaO/Al}_2\text{O}_3$ as a function of temperatures with CO (Δ) or C_3H_8 (\square) as reductant.

the catalyst. Both outlet NO_2 and NO concentrations decreased to zero immediately after switching. As seen in figure 2a, the NH_3 concentration in the outlet stream reached levels higher than 500 ppm, which would be the expected concentration if the entire NO in the feed was reduced into NH_3 . This shows that the released NO_x , which was stored in LNT catalyst during the lean cycle, also participated in the NH_3 formation when the operation was switched to the rich cycle.

Lean–rich cyclic operations over $\text{Pt-BaO/Al}_2\text{O}_3$ catalyst were performed in the entire temperature range of 260–600 °C using CO and C_3H_8 , respectively, to explore the effect of steam on the NO_x conversion and the NH_3 formation during the rich cycle. Figure 2b shows the NO_x conversion and NH_3 selectivity as a function of temperature. There is no apparent difference for NO_x conversion between the two types of reductants, and the NO_x conversion depends simply on the operation protocol. Compared with <3% NO conversion at 260 °C under rich steady-state condition shown in figure 1b, the rich NO_x period conversion at the same temperature under lean–rich cyclic operation jumped to approximately 50% for both reductants and the light-off temperature for cyclic operation decreased by ~60 °C. The NO_x conversion increased with temperature until

reaching a maximum of 90% at ~360 °C. Unlike the complete conversion obtained at high temperature steady-state conditions (figure 1b), under cyclic operations the NO_x conversion slightly decreased with increase in temperature beyond 360 °C, but still remained above 82% in the range of 300–600 °C.

A big difference between rich steady-state and lean–rich cyclic operation was seen in the NH_3 selectivity in the presence of steam. When CO was used as reductant, the NH_3 selectivity ($S_{\text{NH}_3}(\text{R})$) under the rich steady-state condition was 100% at 260 °C, and then gradually decreased to 90% as the temperature increased to 500 °C, and finally dropped down to 44% at 616 °C. However, under cyclic operations, the maximum NH_3 selectivity ($S_{\text{NH}_3}(\text{R/L} + \text{R})$) during the rich cycle was 56%, as shown in figure 2b. The NH_3 selectivity was only 17% at 260 °C, and increased quickly to 46% when the temperature increased to 315 °C. Upon further temperature increase in the range of 315 to 615 °C, the NH_3 selectivity ranged between 46 and 56%. It should be noted that under both steady-state and cyclic conditions, the NH_3 selectivity was the same i.e. 44% when temperature reached 615 °C. When C_3H_8 was used as reductant, the NH_3 selectivity as a function of temperature increased with increase of reaction temperature, as

shown in figure 2B. Compared to the results under rich steady-state (figure 1B), the selectivity trends were similar, but at consistently lower values.

3.3. Temperature-programmed reduction characterization of stored NO_x over Pt–BaO/Al₂O₃ under H₂ atmosphere

The formation of NH₃ in the presence of steam, NO_x, and CO or C₃H₈ must be attributed to reactions among H₂O, NO_x, and CO or C₃H₈. A reasonable explanation for the observed difference in NH₃ selectivity between CO and C₃H₈ as reductant is that in both cases hydrogen is formed as an intermediate, followed by the reduction of NO_x with hydrogen leading to the formation of ammonia. The following evidences would support our hypothesis:

- (1) For the H₂ + NO system under dry or steam atmosphere, our NO reduction experiments (not shown here) and the very recent results of Fridell's group [8] demonstrated that hydrogen is a cause of NH₃ formation over Pt–BaO/Al₂O₃ catalyst.
- (2) For the CO + NO system under dry atmosphere, NCO species can be observed by IR spectroscopy over Pt/Al₂O₃ [13, 15] and Pt–BaO/Al₂O₃ [25]. Nevertheless, Shelef *et al.* found that most of the isocyanate is adsorbed on the Al₂O₃ surface and not on Pt [12]. For the CO + NO system under steam atmosphere, gaseous isocyanic acid (HNCO) was detected over Pt/SiO₂ [16, 18]. However, HNCO was never observed over Pt/Al₂O₃ for the NO + CO + H₂O system. Furthermore, gaseous hydrogen was detectable especially in presence of sufficient steam [16, 18]. Therefore, the authors stated that water–gas shift is forming surface H atoms as the first step of ammonia formation over Pt/Al₂O₃ [18].
- (3) For the H₂ + NO + CO system, no cyanates were detectable when a Pt/Al₂O₃ catalyst was used: instead ammonia was observed and it was, therefore, assumed that ammonia stems from the hydrolysis of cyanates [11].
- (4) It is well known that both the water gas shift reaction (CO + H₂O → CO₂ + H₂) [26–28], hydrocarbon steam reforming (C₃H₈ + 3H₂O → 3CO + 7H₂) [29], and the catalytic reduction of NO by H₂ [9–11] can occur over Al₂O₃-supported Pt catalysts. If NH₃ is formed through hydrogen as a “bridging” intermediate for the CO + H₂O + NO system, it would be reasonable to assume that the ammonia formation for the C₃H₈ + H₂O + NO system also occurs through hydrogen as intermediate. On the other hand, it is recognized that NO₂ exposure to BaO/Al₂O₃ forms Ba(NO₃)₂ [2, 24, 30, 31] and the released product from Ba(NO₃)₂ decomposition is NO_x [24, 30, 32–34]. In order to demonstrate the possibility that the NH₃ comes

from hydrogen and what role the NO_x stored during the rich condition plays, and further to demonstrate whether the NH₃ is derived from the reaction of H₂ with NO_x or the reaction of H₂ with nitrate, temperature-programmed reduction (TPR) experiments were performed using hydrogen (5% H₂/N₂) as reducing agent. Figure 3 shows the differential thermogravimetric (DTG) curves. Two weight loss peaks were found in the DTG curves, located at 151 °C and 212 °C, respectively. The occurrence of two weight loss peaks is attributed to the release of two different nitrate species: dispersed and bulk-like, which are formed by NO₂ with BaO. The reasons for the peak assignment are that two thermal events were also observed for the thermal decomposition of Ba(NO₃)₂/Al₂O₃ under 5% H₂/N₂ (not shown here) and the assignment of the two thermal peaks for the thermal release of stored NO₂ over BaO/Al₂O₃ has been demonstrated with different ramp rates under N₂ atmosphere [24]. The release peaks of stored NO_x over Pt–BaO/Al₂O₃ model catalyst under N₂ atmosphere with the same heating rate (10 °C/min) were observed at 454 and 513 °C, respectively. Since the release peaks of 151 and 212 °C under H₂ atmosphere occur at much lower temperatures than those under N₂ atmosphere, it is unlikely that they are related to the thermal release of NO_x from nitrate. Instead, they indicate a direct reduction of stored NO_x (nitrate) by hydrogen, most likely catalyzed by Pt. It is interesting that the peak gap between the dispersed and bulk-like phases is the same, i.e. approximately 60 °C, regardless of the atmosphere applied, showing that the difference of stability of different types of nitrates is similar under different atmospheres.

In order to demonstrate that the two DTG peaks result from the release of stored NO_x or from the reduction of stored NO_x by H₂, the gases evolved from TGA were measured on-line by IR during the TGA heating ramp. Unlike the case under N₂ atmosphere, the gases evolved under H₂ atmosphere did not contain any NO and NO₂, and the only N-containing species observed was NH₃. In addition to weak IR bands in the range of 3974–3474 cm^{−1} (assigned to H₂O vapor), very strong vibration band pairs located at 965 and 930 cm^{−1} (assigned to NH₃) were observed. These results are quite different from those reported by Liu *et al.* [5], who observed NO_x evolution along with the reduction product N₂. In their case, the ratio of NO to NO₂ and the peak positions of NO_x released under reducing atmospheres were affected by the types of reductants (H₂, CO, C₃H₆). In our case, as shown in figure 3, the peak positions (170 and 218 °C) of integrated NH₃ bands, whose intensities correspond to the gaseous NH₃ concentration evolved from TGA, were very close to the DTG release peaks (151 and 212 °C). Thus the

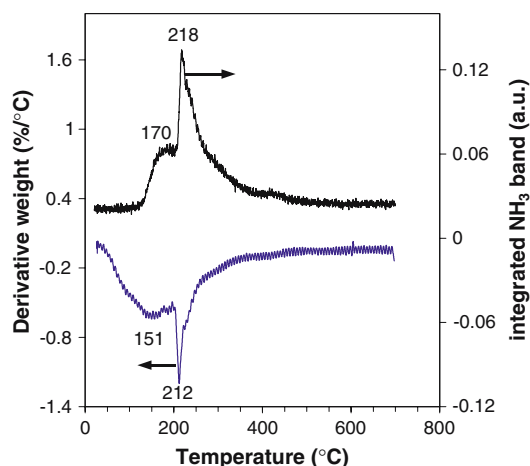
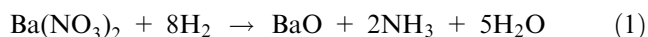
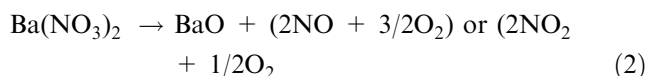


Figure 3. Derivative thermogravimetric (DTG) curve and integrated IR band of evolved NH₃ during the release of stored NO₂ over Pt–BaO/Al₂O₃ under dry H₂ atmosphere (5% H₂/N₂).

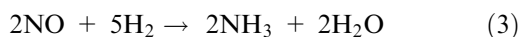
occurrence of NH₃ resulting from the direct reduction of NO₃[−] by H₂ might be presented by the reactions of



When compared with the decomposition temperatures under N₂ atmosphere, the much lower weight loss peak temperatures under H₂ atmosphere do not support the occurrence of decomposition of Ba(NO₃)₂ according to

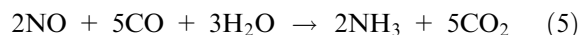


According to the decomposition thermodynamics and kinetics, the decomposition temperature of Ba(NO₃)₂ should not depend on the atmosphere applied unless the atmosphere itself participates in reactions facilitating the Ba(NO₃)₂ decomposition. Furthermore, the following reactions 3 and 4, which are among the five steps in the LNT model reaction [3], do most likely not apply for stored NO_x (i.e. nitrate) during heating of TGA because reaction 2 does probably not occur under H₂.



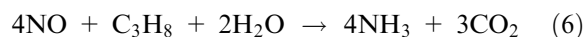
Therefore, according to previous literatures and our TGA-IR and reaction results, the NH₃ formation in sufficient steam (10% water) over Pt–BaO/Al₂O₃ could be attributed to the generation of hydrogen over Pt sites [16, 18]. Some portion of NH₃ is probably derived from direct reaction of generated hydrogen with NO in the feed to form ammonia based on equation (3) or through a proposed mechanism of NCO or HNCO as an

intermediate as reported previously [11, 13, 15, 18]. Other portion of NH₃ should be attributed to the direct catalytic interaction of hydrogen with stored NO_x according to reaction (1). When CO is used as reductant, the relationship between NH₃ selectivity and reaction temperature could be well explained by the water gas shift (WGS) reaction because the reaction characteristic of NH₃ formation during rich conditions in our experiments are very consistent with H₂ generation of WGS over Pt/Al₂O₃ catalyst. It is well known that the WGS conversion decreases with temperature at temperatures above 500 °C [26–28]. Furthermore, WGS (CO + H₂O ↔ H₂ + CO₂) is exothermic (ΔH₂₉₈⁰ = −41.2 kJ/mol) and reversible. It requires low temperature for high equilibrium conversion because H₂ generation is unfavorable at high temperature. The experimental results for NH₃ formation versus temperature (figures 1b and 2b) are consistent with the hydrogen generation from WGS over Al₂O₃-supported Pt catalyst [26–28]. This would lead to an overall reaction of:



However, we cannot exclude the NH₃ formation via NCO as intermediate as proposed in previous publications [11, 13, 15–18] with CO as reductant.

When C₃H₈ is used as reductant, the effect of steam could well be interpreted by the NH₃ formation due to NO reduction with hydrogen. The relationship between NH₃ selectivity and reaction temperature is consistent with the H₂ generation through hydrocarbon reforming over Al₂O₃-supported Pt catalyst. Propane steam reforming (C₃H₈ + 3H₂O → 7H₂ + 3CO) is an endothermic (ΔH₂₉₈⁰ = 497.7 kJ/mol) reaction. Thus, high temperature favors H₂ production. Because H₂ is a more effective reducing agent than C₃H₈, the NH₃ selectivity increases with increasing reaction temperature. Steam reforming of C₃H₈ as a function of temperature can account for the results shown in figures 1b and 2b, and leads to an overall reaction of:



3.4. NO_x reduction over dual bed system under lean–rich cyclic conditions

From the viewpoint of environmental protection, replacing automotive NO_x exhaust emissions with NH₃ emissions is not an acceptable solution. Therefore, an initial effort for the elimination of NH₃ over LNT Pt–BaO/Al₂O₃ model catalyst has also been made in this work. It was found that NH₃ could be effectively removed from the exhaust when a dual bed reactor was applied in the lean–rich operations, with an equal-weight Co²⁺-exchanged Beta zeolite (Co²⁺-Beta) bed

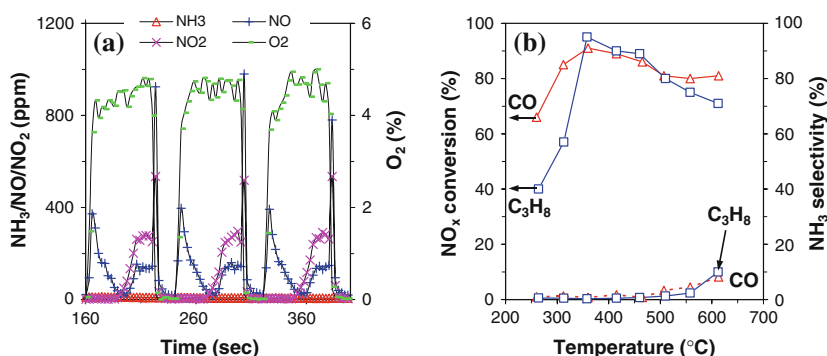


Figure 4. (a) Exit gas concentration of stabilized lean-rich cycles at 360 °C for NO_x trapped and reduced by CO over a dual bed system of 100 mg Pt–BaO/Al₂O₃ followed by 100 mg Co²⁺-Beta catalysts using lean (500 ppm NO-10% H₂O-10% CO₂-5% O₂-balance N₂) and rich (500 ppm NO-10% H₂O-10% CO₂-1.7% CO-balance N₂) cycles (L/R = 60/20 s); (b) NO_x conversion (solid line) and NH₃ selectivity (dashed line) during rich cyclic period over dual bed as a function of temperature with CO (Δ) or C₃H₈ (□) as reductant.

placed downstream of the Pt–BaO/Al₂O₃ bed. Figure 4a shows the outlet gas concentration from the dual bed when CO was used as reductant under lean-rich cyclic operation at 360 °C with L/R = 60/20 (s/s). It is apparent that the use of the combination of LNT model catalyst with Co²⁺-Beta effectively eliminates the NH₃ emissions. No NH₃ was detected by mass spectrometry during the entire lean-rich cyclic time. Comparing figure 2a with figure 4a, it should be noted that in the dual bed operation some NO is formed at the beginning of the lean period. This can probably be attributed to the oxidation of adsorbed NH₃ by O₂ according to the reaction of $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$.

In order to evaluate the function of Co²⁺-Beta in the whole temperature range, the same L/R operation protocols described above were performed over the dual bed reaction system. Figure 4b compares the NH₃ selectivity in the rich cyclic mode when CO and C₃H₈ were used as reductants, respectively. As compared to the results over a single bed (Pt–BaO/Al₂O₃) as shown in figure 2b, the NH₃ selectivity dramatically decreased within the rich period regardless of whether CO or C₃H₈ was used. The NH₃ concentration with the dual bed system was close to zero until the reaction temperature exceeded 500 °C. We believe that Co²⁺-Beta functions as an adsorbent, retaining the NH₃ formed in the first bed. There are two types of evidence for this hypothesis. Firstly, when L/R operation was run at temperatures above 500 °C with L/R = 60/20 (s/s), small concentrations of NH₃ started to appear for both CO and C₃H₈ reductants, as shown in figure 4b. This indicates the limited performance of Co²⁺-Beta at temperatures higher than 500 °C. The amount of NH₃ generated through NO_x reduction by H₂ over Pt–BaO/Al₂O₃ may be beyond the adsorption capacity of Co²⁺-Beta because high temperature does not favor the adsorption of NH₃ on zeolites. Secondly, the effectiveness of Co²⁺-Beta to remove NH₃ was decreased when the rich cyclic time was prolonged to beyond 20 s. When the rich cyclic time was prolonged while keeping the lean period

duration constant at 60 s, the dual bed outlet NH₃ concentration in the rich cycle increased until a rich period duration of 60 s, where the NH₃ concentration leveled off at a stable value. At rich period durations beyond 60 s, the performance of the dual bed started to closely resemble that of the single bed Pt–BaO/Al₂O₃ under rich steady-state (shown in figure 1B). This is illustrated in figure 5, showing the performance of the dual bed for L/R = 60/1800 (s/s) as a function of temperature. Therefore, when the rich cyclic time was prolonged to more than 20 s, the amount of NH₃ generated over Pt–BaO/Al₂O₃ was again beyond the adsorption capacity of the Co²⁺-Beta zeolite.

However, for the case of short rich cycle periods (< 20 s) the question remains what happens to the NH₃ stored in Co²⁺-Beta when switching from rich to lean. There is no NH₃ desorption or release observed in the outlet of the dual bed reactor, as shown in figure 4a.

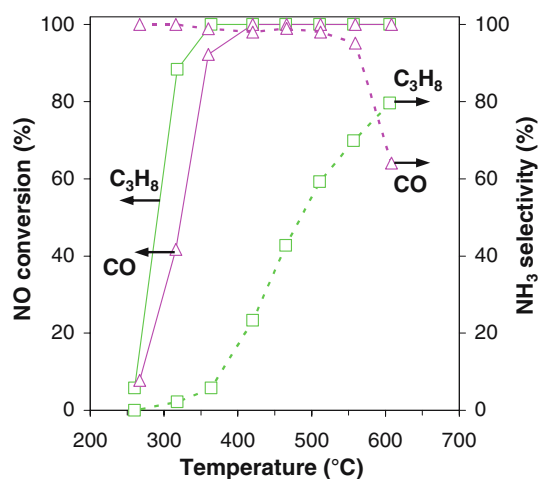


Figure 5. NO_x conversion (solid line) and NH₃ selectivity (dashed line) during rich cyclic period for NO_x trapped and reduced over dual bed system with CO (Δ) or C₃H₈ (□) as reductant; the reaction was run under lean-rich (L/R = 60s/1800s) cyclic operations with other conditions the same as in Figure 4.

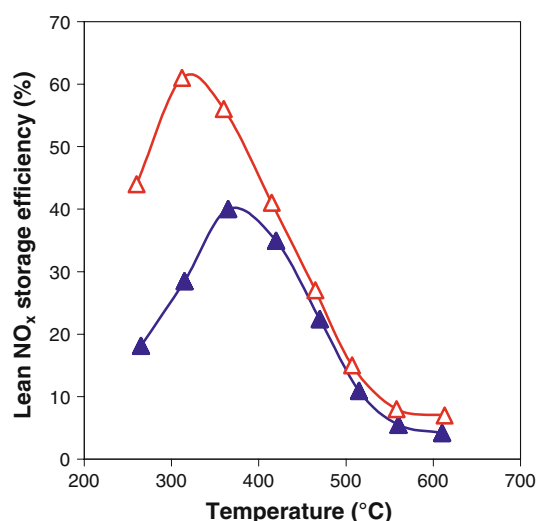


Figure 6. Comparison of lean NO_x storage efficiency during lean cyclic period for NO_x trapped and reduced with CO as reductant over single LNT model catalyst (▲) and dual bed system (Δ) using lean–rich cycle operations the same as in figure 4.

This phenomena may be reasonably interpreted by assuming that NH₃ stored on Co²⁺-Beta in turn is oxidized by NO or O₂ during the lean cycle, according to $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$. Figure 6 shows a comparison of the lean NO_x storage efficiency (defined as NO_x removal percent during lean period) over Pt–BaO/Al₂O₃ and the dual bed system, respectively. It is apparent that at temperatures below 450 °C, the adsorbed NH₃ probably participates in NO_x reduction over Co²⁺-Beta and hence promotes the total NO_x elimination during the lean cycle. In fact, the NH₃-SCR is currently utilized as the preferred reducing agent for the lean NO_x control in exhaust emissions due to its unique high activity and selectivity toward NO_x abatement [35]. However, at temperature higher than 450 °C, it seems that the NH₃ oxidation by O₂ dominates.

4. Conclusions

The steam impact cannot be ignored, as it significantly affects the product composition for lean NO_x elimination over LNT Pt–BaO/Al₂O₃ model catalyst during the rich cycle period. The presence of steam in the reaction system results in the generation of NH₃. Temperature-programmed reduction on NO₂ exposed Pt–BaO/Al₂O₃ by thermogravimetry (TG) coupled with infrared spectrometry (IR) demonstrated that the NH₃ generation stems from NO_x reduction by H₂. We believe that under steam atmosphere, hydrogen is produced via the water gas shift reaction when CO used as reductant; or via steam reforming when C₃H₈ used as reductant. Both of these reactions are catalyzed by Al₂O₃-supported Pt, and the hydrogen in turn selectively catalyzes NO_x reduction to NH₃ over Al₂O₃-supported Pt. The

NH₃ formed can be effectively eliminated by a dual bed catalyst system combining the LNT model catalyst with a second bed containing Co²⁺-Beta. This dual bed system with Co²⁺-Beta can completely trap NH₃ at temperatures below 500 °C, as long as the duration of the rich cycle is shorter than 20 s. The NH₃ stored during the rich cycle is then used during the lean cycle to selectively reduce NO_x to N₂ over Co²⁺-Beta. Thus, during the lean cycle, both NO_x and NH₃ can be effectively removed from the exhaust at temperatures lower than 450 °C.

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